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Low-temperature (210 °C) deposition of crystalline germanium via in situ disproportionation of GeI_2

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ABSTRACT

A new approach is reported for depositing crystalline germanium films. The deposition occurs at low temperatures (210–260 °C) via in situ disproportionation of GeI_2 and is thereby useful for depositing Ge onto a wide range of surfaces. Deposition onto glass and polymer substrates is demonstrated. The rate of deposition onto glass is found to be 25 ng min^{-1}. New synthetic routes to GeI_2, GeI_4, and Cu_3Ge are also reported. These are valuable precursors for the synthesis of germanium nanostructures and organogermanium compounds.

1. Introduction

Interest in using germanium thin films for photonic applications and telecommunications has steadily increased due to its high refractive index [1] and strong absorption at optical wavelengths near 1.55 μm [2,3]. Germanium has long been used for various types of photodetectors [4], and has also been shown to be useful as a filter for short-wave infrared [1]. It has the additional feature of being compatible with silicon and silicon-based optoelectronics [3–5], so it can be integrated into existing materials processes [5]. Two-dimensional photonic crystals with functional stop bands at telecommunication wavelengths have been created in germanium supported on SiO_2-on-Si substrates [6]. The optical properties of germanium support efficient light emission and optical gain [7], which has enabled the development of an integrated Ge-on-Si laser [8]. Traditional methods for depositing germanium onto a substrate include chemical vapor deposition (CVD) [9], ultrahigh vacuum CVD [3], rapid-thermal CVD [10], plasma-enhanced CVD [11], and sputtering [1,12]. These methods utilize digermane (Ge_2H_6) [9], germane (GeH_4) diluted in H_2 gas, or in situ disproportionation of germanium diiodide (GeI_2) synthesized from the elements [13]. The disadvantage of these techniques is that germanes are toxic and unstable, and I_2 is corrosive. In addition, these methods require temperatures between 280 and 550 °C to obtain crystalline germanium [10,14], as processing at lower temperatures yields amorphous material [9,14].

GeI_2 has been previously synthesized by reacting Ge with GeI_4 [15,16] or I_2 [13]. If excess I_2 is used, the formation of the tetraiodide is favored [15]. Alternatively, germanium sulfide has been reacted with silver halides to obtain the tetrahalide as the major product. Analogous to this is the formation of $SiCl_4$ synthesized from Si and CuCl [17,18]. The tetraiodide is favored in this case. A similar reaction was carried out using lead halides [19]. Other methods have been reported that yield a mixture of iodides [13].

The current study introduces a new in situ synthesis and disproportionation of GeI_2 that enables low temperature deposition of germanium, even onto a polymeric surface. Previously, disproportionation of GeI_2 to Ge and GeI_4 was shown to occur at ~330 °C [20], but we show here that this can be made to occur between 210 and 260 °C to form polycrystalline germanium films.

2. Experimental

2.1. Reagent preparation

Copper iodide was used as received (Acros Organics, 98%). Germanium (Alfa Aesar, 99.999%) was mechanically ground in a tungsten carbide vial with four tungsten carbide ball bearings

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(1.27-cm dia.) for 30 min using a SPEX 8000M Mixer/Mill. The resulting powder was sieved to 270 mesh. CuI and Ge were mixed in stoichiometric quantities by grinding for 5 min.

2.2. Substrates for germanium deposition

Germanium was deposited onto either borosilicate glass microscope slides or slides supporting a film of cross-linked SU-8 polymer, hereafter referred to as the "sample". Sample sizes of 25 mm × 25 mm and 38 mm × 25 mm were used. Borosilicate microscope slides were cleaned in a 50/50 by-volume solution of concentrated nitric and sulfuric acid for 2 h, rinsed with copious deionized water, then dried in an oven at 100 °C for 20 min.

2.3. Polymer film preparation

An adhesion layer was applied to a cleaned substrate by immersing it into 5 vol.% 3-glycidoxypropyl-trimethoxysilane (98%, CAS# 2530-83-8) in methanol for 24 h at room temperature, rinsing with methanol, and drying for 1 h in an oven at 100 °C. The pre-polymer resin SU-8 2035 (MicroChem) consisted of 70–80 wt.% of the cross-linkable epoxide SU-8 (CAS# 28906-96-9) and 3.4 wt.% of two triarylsulfonium photo-acid generators (CAS# 89452-37-9 and 71449-78-0), dissolved in a mixture (circa 19 wt.% volatiles) of cyclopentanone (CAS# 120-92-3) and propylene carbonate (CAS# 108-32-7). A 1 mL portion of filtered resin (0.4 μm pore) was dispensed onto the substrate and spin-coated according to the following program: ramp at 100 rpm s^{-1} to 500 rpm, hold for 10 s, ramp at 300 rpm s^{-1} to 1400 rpm, hold for 30 s, then stop. Surface profilometry measurements indicate that this procedure yields films having a thickness of 30 ± 5 μm. Following spin-coating, the slides were heated on a hot plate at 65 °C for 15 min, 95 °C for 2 h, 65 °C for 15 min, then removed from the hot plate and allowed to cool to room temperature. The films were then irradiated for 2 min in a Zeta Loctite UV system (RPR 3500 Å lamps, emission maximum at 350 nm) equipped with a long-pass filter (Omega Optical PL-360LP, 350 nm cut-off). Following exposure, the films were baked on a hot plate at 65 °C for 1 min, 95 °C for 15 min, hard-baked at 250 °C for 12 h, then removed and allowed to cool to room temperature.

2.4. Reaction vessel

A borosilicate glass sublimation tube was used as the reactor vessel for germanium deposition (Fig. S1). The samples were affixed in a holder consisting of an adjustable-height clip mounted on a base constructed from steel, graphite, or quartz. The reagents were loaded into a borosilicate vial in a glove box. The reagent vial and the sample were inserted into the reaction vessel, removed from the glove box, and inserted into a three-zone tube furnace (Lindberg Hevi-Duty 54357-A, 76.5 cm length). Zone one was used to control the temperature of the sample. Zone two served as a hot zone that initiates formation of GeI_2 upon reaction of the solid reagents. Zone three was not used. The temperatures of zones one and two (length 15 cm and 29 cm, respectively) were monitored with K-type thermocouples positioned 22.3 cm and 35 cm from the end of the furnace and connected to an ADAM-4019+-AE eight-channel universal analog input module (Advantech Co., Ltd.). Temperature data were logged with a computer running LabView. Heat transfer was reduced by placing mineral wool insulation between zones one and two, at 22.8–25.0 cm from the end of the furnace. The sample was positioned in zone one at a distance from the end of the furnace adjustable between 18.5 cm and 22.3 cm. The reagent vial was centered within zone two. Dynamic vacuum was applied for 1 h with a two-stage rotary vane pump, reducing the pressure to 330 mTorr. The system was closed to vacuum after 1 h to prevent contamination of the line by germanium iodides. Deposition was initiated by heating zone two to 75 °C over 15 min, then increasing to a final set point of 175 °C, while zone one was heated to 400 °C. The reaction was allowed to proceed overnight in most cases.

2.5. Deposition rate measurements

A quartz crystal microbalance (QCM) was used to determine the rate of germanium deposition. For these measurements, the sample slide was replaced by a quartz crystal. The temperature near the crystal and its resonant frequency were measured as Ge deposited onto it. One thermocouple was placed between the crystal and the sample holder. The reaction vessel was fitted with an aluminum cap equipped with a vacuum tap and three electrical feedthroughs for the thermocouples and leads to the crystal. The thermocouple and crystal leads were insulated with single-hole fish spline and sealed with epoxy and Celva-2 sealant (Duniway Stockoom Corp.). Data were measured using a Princeton Applied Research QCM922 and WinEChem software at 10 s intervals over 18 h, with a scan frequency $\nu = 9.00$ MHz, $\Delta\nu = \pm 20$ kHz, and a gate time of 1 s. The QCM response versus temperature was calibrated by performing a blank run for 18 h with only Ge powder loaded into the reagent vial.

2.6. Characterization

Powder X-ray diffraction (XRD) data were collected using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu Kα, $\lambda = 1.5418$ Å). Diffractograms were collected over a 2θ angle of 5–80° using 0.010° steps and a dwell time of 0.3 s per step. The morphology of deposited Ge was characterized by scanning electron microscopy (SEM, Zeiss ULTRA-55 FEG SEM, 2.5–5.0 kV accelerating voltage).

3. Results and discussion

While heating stoichiometric quantities of CuI and Ge at 400 °C under vacuum, we observed that yellow GeI_2, red GeI_4, and reflective germanium deposit in bands on the walls of the reactor tube (Fig. 1). Germanium deposited in regions of zone one where the temperature was near 210 °C. No germanium deposited in zone two, where the temperature was 260–400 °C, or in regions further along the reaction vessel that were cooler than 210 °C. GeI_2 can form initially in the hot-zone from the reaction between Ge and CuI, as described by Eq. (1).

$$5Ge + 6CuI \rightarrow 3GeI_2 + 2Cu_3Ge \tag{1}$$

This suggests there is a narrow temperature region where GeI_2 disproportionation to Ge and GeI_4 is favored. These observations led us to investigate the possibility of depositing Ge onto glass and polymer substrates.

The X-ray diffractogram for Ge deposited onto a polymer substrate is shown in Fig. 2. The deposited material is composed mainly of polycrystalline Ge with a small impurity of CuI. Unreacted CuI can sublime from the hot-zone and deposit in the cooler zones, mostly above the band where Ge forms, although some can co-deposit onto the sample. The diffractograms show that this surface impurity is easily removed by washing the sample with acetonitrile.

The morphology of germanium deposited onto glass slides was examined by SEM and is shown in Figs. 3 S2, and S3. Deposition is initially uniform, but as the reaction proceeds, polycrystalline Ge begins to form. Growth on existing crystals appears to dominate over nucleation. This is consistent is observed for growth of germanium on silicon surfaces [21].